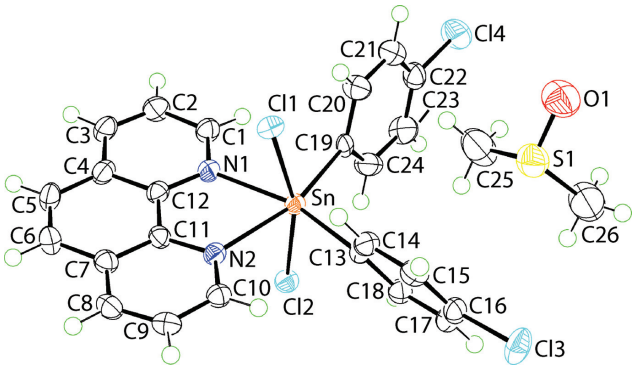
Kong Mun Lo, See Mun Lee and Edward R.T. Tiekink*

Crystal structure of *trans*-dichloridobis(4-chlorophenyl-κC^1)(1,10-phenanthroline-κ$^2N,N'$)tin(IV) dimethylsulphoxide solvate, $C_{26}H_{22}Cl_4N_2OSSn$



https://doi.org/10.1515/ncrs-2020-0302
Received June 19, 2020; accepted July 10, 2020; available online July 24, 2020

Abstract

$C_{26}H_{22}Cl_4N_2OSSn$, triclinic, $P\bar{1}$ (no. 2), $a = 8.2966(1)$ Å, $b = 11.4971(2)$ Å, $c = 14.3311(2)$ Å, $\alpha = 90.322(2)°$, $\beta = 101.783(1)°$, $\gamma = 95.780(1)°$, $V = 1330.91(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0258$, $wR_{ref}(F^2) = 0.0684$, $T = 100$ K.

CCDC no.: 2015488

The molecular structures are shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

Tetra(4-chlorophenyl)tin was synthesized from the reaction of stannic chloride (Fluka) with 4-chlorophenylmagnesium bromide (Fluka) in a 1:4 molar ratio. Subsequently, di(4-chlorophenyl)tin dichloride was synthesized from the comproportionation reaction of tetra(4-chlorophenyl)tin with stannic chloride (Fluka) in a 1:1 molar ratio to obtain a white precipitate. Di(4-chlorophenyl)tin dichloride (0.41 g, 1.0 mmol) and 1,10-phenanthroline (Sigma-Aldrich; 0.18 g, 1.0 mmol) were heated in 95% ethanol (30 mL) for 1 h with stirring. After filtration, the filtrate was evaporated slowly until white compounds were formed. The compound was recrystallised from its dimethyl sulphoxide solution. The solution was evaporated slowly until colourless crystals were formed.

Yield: 0.25 g (37%). **M.pt** (Mel-temp II digital melting point apparatus): 549–551 K. **IR** (Bruker Vertex 70v FTIR Spectrophotometer; cm^{-1}): 1475 (m) ν(C-C), 1008 (s) ν(S=O), 487(m) ν(Sn-N). **^{1}H NMR** (Bruker Ascend 400 MHz NMR spectrometer; DMSO-d_6; p.p.m. relative to Me_4Si): 2.50 (s, 6H, Me), 7.10–7.28 (m, 4H, Ph-H), 7.35–7.80 (m, 10H, Ph-H), 8.10–8.22 (m, 2H, Ph-H). **^{13}C{^{1}H} NMR** (as for ^{1}H NMR): 41.0 (Me), 124.9, 126.9, 127.7, 128.4, 129.5, 136.3, 137.8, 138.9, 142.0, 149.8 (Ph–C).

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.08 × 0.07 × 0.03 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ:	12.3 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max}, completeness:	67.1°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	31273, 4736, 0.043
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4566
$N(param)_{refined}$:	318
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.95–0.98 Å) and refined as riding with $U_{iso}(H) = 1.2$–$1.5U_{eq}(C)$.

Comment

The simple formation of diorganotin dihalide adducts with chelating bipyridine-type molecules (NN), i.e. molecules conforming to the general formula $R_2SnX_2(NN)$, mask unresolved structural issues relating to geometric isomerism. Thus, in the $C_2Cl_2N_2$ octahedral geometries, both cis-Cl_2 and trans-Cl_2 geometries are observed. These structural issues are nicely exemplified by structures closely related to the title compound, i.e. $(4\text{-}ClC_6H_4)_2Sn(NN)Cl_2$ for NN = 4,4′-dimethyl-

***Corresponding author: Edward R.T. Tiekink,** Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia, e-mail: edwardt@sunway.edu.my. https://orcid.org/0000-0003-1401-1520
Kong Mun Lo and See Mun Lee: Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Open Access. © 2020 Kong Mun Lo et al., published by De Gruyter. This work is licensed under the Creative Commons Attribution 4.0 International License.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Sn	0.36930(2)	0.30312(2)	0.66369(2)	0.01552(7)
Cl1	0.58737(7)	0.31493(5)	0.56764(5)	0.02063(14)
Cl2	0.09880(7)	0.26656(5)	0.71406(5)	0.02011(13)
Cl3	0.52383(10)	0.86349(6)	0.81157(5)	0.03120(16)
Cl4	0.82578(10)	0.06247(7)	1.03909(6)	0.03801(18)
N1	0.2863(3)	0.12878(18)	0.57746(16)	0.0184(4)
N2	0.2061(3)	0.33982(18)	0.51583(16)	0.0169(4)
C1	0.3322(3)	0.0264(2)	0.6092(2)	0.0218(6)
H1	0.394660	0.022332	0.672256	0.026*
C2	0.2909(4)	−0.0759(2)	0.5519(2)	0.0254(6)
H2	0.326125	−0.147958	0.576092	0.030*
C3	0.2003(3)	−0.0718(2)	0.4617(2)	0.0246(6)
H3	0.171920	−0.140975	0.422707	0.029*
C4	0.1486(3)	0.0354(2)	0.4262(2)	0.0215(5)
C5	0.0530(3)	0.0485(2)	0.3320(2)	0.0252(6)
H5	0.020092	−0.018062	0.290398	0.030*
C6	0.0090(3)	0.1548(3)	0.3016(2)	0.0250(6)
H6	−0.055669	0.161384	0.239344	0.030*
C7	0.0590(3)	0.2574(2)	0.3624(2)	0.0200(5)
C8	0.0235(3)	0.3704(2)	0.3326(2)	0.0225(6)
H8	−0.040011	0.381467	0.270766	0.027*
C9	0.0818(3)	0.4642(2)	0.3940(2)	0.0216(5)
H9	0.060517	0.541032	0.374709	0.026*
C10	0.1728(3)	0.4459(2)	0.4855(2)	0.0187(5)
H10	0.212197	0.511567	0.527386	0.022*
C11	0.1514(3)	0.2466(2)	0.45509(19)	0.0175(5)
C12	0.1961(3)	0.1346(2)	0.48790(19)	0.0179(5)
C13	0.4036(3)	0.4873(2)	0.70437(19)	0.0164(5)
C14	0.4987(3)	0.5674(2)	0.6606(2)	0.0208(5)
H14	0.540881	0.542577	0.607824	0.025*
C15	0.5335(3)	0.6834(2)	0.6927(2)	0.0224(6)
H15	0.597244	0.737702	0.661466	0.027*
C16	0.4742(3)	0.7188(2)	0.7704(2)	0.0216(6)
C17	0.3787(3)	0.6415(2)	0.8166(2)	0.0215(5)
H17	0.338752	0.666654	0.870063	0.026*
C18	0.3433(3)	0.5264(2)	0.7824(2)	0.0202(5)
H18	0.276664	0.472931	0.812566	0.024*
C19	0.5097(3)	0.2137(2)	0.78222(19)	0.0181(5)
C20	0.6772(4)	0.1961(3)	0.7825(2)	0.0262(6)
H20	0.723278	0.216779	0.728690	0.031*
C21	0.7740(4)	0.1488(3)	0.8614(2)	0.0284(6)
H21	0.885270	0.135597	0.861585	0.034*
C22	0.7046(4)	0.1213(2)	0.9395(2)	0.0260(6)
C23	0.5435(4)	0.1386(3)	0.9405(2)	0.0298(6)
H23	0.497990	0.119328	0.994788	0.036*
C24	0.4474(4)	0.1850(3)	0.8602(2)	0.0270(6)
H24	0.335709	0.196495	0.860426	0.032*
S1	0.87717(10)	0.62990(7)	0.88798(6)	0.03572(18)
O1	1.0591(3)	0.6200(2)	0.90976(19)	0.0444(6)
C25	0.7802(5)	0.4842(3)	0.8759(3)	0.0483(9)
H25A	0.808993	0.444670	0.821750	0.072*
H25B	0.659833	0.485292	0.865036	0.072*
H25C	0.818189	0.442254	0.934347	0.072*
C26	0.8222(5)	0.6689(4)	0.9972(3)	0.0538(10)
H26A	0.865773	0.615351	1.046895	0.081*
H26B	0.701339	0.663516	0.988386	0.081*
H26C	0.869202	0.749140	1.016443	0.081*

2,2′-bipyridyl [5]. For the unsolvated form of the molecule, isolated from ethanol solution, the commonly observed form [6, 7], with a cis-disposition of Cl atoms is formed. Spectroscopy showed that recrystallisation from each of methanol and dimethylformamide solutions gave the trans form which could be converted back to the cis form from toluene. Despite this, two distinct toluene solvates had the organotin molecule with a trans-disposition of the Cl atoms [5]. In continuation of on-going structural studies in this area [8, 9], recently the crystallographic characterisation of $(4\text{-}ClC_6H_4)_2Sn(1,10\text{-phenanthroline})Cl_2$ was described [10], which had the commonly observed cis-dispositon of Cl atoms; this was isolated from ethanol solution. Subsequently, recrystallisation of this compound from dimethyl sulphoxide (DMSO) afforded the title 1:1 DMSO solvate, (I). Herein, its crystallographic characterisation is described.

The molecular structure of (I) is shown in the figure (50% displacement ellipsoids). The Sn atom is coordinated by two cis-ipso-C atoms, derived from the 4-chlorophenyl substituents, two trans-Cl atoms and two cis-N atoms derived from the chelating 1,10-phenanthroline molecule. The resultant $C_2Cl_2N_2$ donor set defines a distorted octahedral geometry. The three trans angles Cl1—Sn—Cl2 [162.76(2)°], N1—Sn—C13 [162.17(9)°] and N2—Sn—C19 [162.03(8)°] show deviations from the ideal 180° but, the greatest deviation from the regular geometry is seen in the N1—Sn—N2 chelate angle of 70.56(8)°. The Sn—Cl bond lengths differ by approximately 0.01 Å [Sn—Cl1 = 2.4812(6) Å & Sn—Cl2 = 2.4918(6) Å], the Sn—N bonds differ by about 0.02 Å [Sn—N1 = 2.316(2) Å & Sn—N2 = 2.335(2) Å] but, the Sn—C bonds are experimentally equivalent [Sn—C13 = 2.168(2) Å & Sn—C19 = 2.180(3) Å]. For comparison, the pairs of Sn—Cl [2.4934(4) & 2.4960(4) Å] and Sn—N [2.3611(15) & 2.3659(15) Å] bond lengths in the unsolvated, cis-Cl form [10] are experimentally equivalent with the Sn—N bonds being longer than in (I), an effect ascribed to the influence of the trans-C atoms. Based on DFT calculations, it has been concluded that non-systematic variations in geometric parameters in compounds of this type arise as a result of molecular packing effects in their crystals [6, 7].

An analysis of molecular packing for (I) showed a variety of non-covalent interactions in operation and the pivotal role DMSO plays in the stabilisation of a three-dimensional architecture. Thus, π—π stacking [shortest contact: Cg(N1,C1–C4,C12)···Cg(C4–C7,C11,C12)^{i} = 3.7619(15) Å, angle of inclination = 1.06(13)° for symmetry operation (i) −*x*, −*y*, 1-*z*], end-on phenyl-C—Cl···π(phenyl) [C16—Cl3···Cg(C19–C24)^{ii} = 3.5314(14) Å with angle at Cl3 = 171.95(10)° for (ii) *x*, 1 + *y*, *z*], C—H···π [shortest contact: C25—H25b···Cg(C13–C18)^{iii} = 2.78 Å with angle at H25b = 133° for (iii) *x*, *y*, *z*] and C—H···O [shortest contact: C17—H17···O1^{iv}:

H17···O1^{iv} = 2.51 Å, C17···O1^{iv} = 3.193(4) Å with angle at H17 = 129° for (iv) $-1+x$, y, z] interactions assemble molecules into a supramolecular layer in the *bc*-plane. The connections between layers are of the type phenyl-C—H···Cl(phenyl) [C23—H23···Cl3^{v}: H23···Cl3^{v} = 2.82 Å, C23···Cl3^{v} = 3.708(3) Å with angle at H23 = 155° for (v) $1-x$, $1-y$, $2-z$] and DMSO-C—H···O(DMSO) [C25—H25c···O1^{vi}: H25c···O1^{vi} = 2.40 Å, C25···O1^{vi} = 3.367(5) Å with angle at H25c = 168° for (vi) $2-x$, $1-y$, $2-z$]. In this scheme, the DMSO molecule forms one C—H···π and three C—H···O contacts.

Additional insight into the molecular packing of (I) was achieved by calculating the Hirshfeld surfaces and two-dimensional fingerprint plots (full and delineated into individual contacts) for the specified asymmetric unit with the aid of Crystal Explorer 17 [11] and as per earlier studies [12]. The major contribution to the surface contacts in the crystal of (I) comes from H···H and Cl···H/H···Cl at 32.8 and 30.9%, respectively. After these are C···H/H···C contacts at 17.4%. The next most significant contribution to the surface contacts are from O···H/H···O, i.e 7.0%, reflecting the importance of C—H···O interactions in the crystal of (I). The latter are obviously lacking from the previously reported unsolvated form of (I) [10], where H···H, Cl···H/H···Cl and C···H/H···C contacts amounted to 29.5, 33.0 and 23.0%, respectively. Contacts of the type C···C and Cl···C/C···Cl, each contributing 6.2%, were also important in the literature structure, but less so in (I), i.e. 3.8 and 3.0%, respectively. The next most significant contributions to the surface contacts in (I) are of the type S···H/H···S [1.7%] and N···H/H···N [1.3%], the remaining contacts contributing less than 1% to the calculated Hirshfeld surface.

Acknowledgements: Sunway University Sdn Bhd is thanked for financial support of this work through Grant No. STR-RCTR-RCCM-001–2019.

References

1. Rigaku Oxford Diffraction: CrysAlis^{PRO}. Rigaku Corporation, Oxford, UK (2018).
2. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
4. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849–854.
5. Kumar Das, V. G.; Keong, Y. C.; Wei, C.; Smith, P. J.; Mak, T. C. W.: The first authenticated example of geometrical isomers in organotin(IV) co-ordination chemistry. the crystal and molecular structures of octahedral cis- and trans-SnR_2 isomeric adducts of dichlorobis(4-chlorophenyl)tin(IV) with 4,4′-dimethyl-2,2′-bipyridyl. J. Chem. Soc., Dalton Trans. (1987) 129–137.
6. Buntine, M. A.; Hall, V. J.; Kosovel, F. J.; Tiekink, E. R. T.: Influence of crystal packing on molecular geometry: a crystallographic and theoretical investigation of selected diorganotin systems. J. Phys. Chem. A **102** (1998) 2472–2482.
7. Buntine, M. A.; Hall, V. J.; Tiekink, E. R. T.: The crystal and molecular structures of R_2SnCl_2(1,10-phenanthroline), R = iPr, Cy, CH_2Ph and R_2 = Me, Ph: a comparison between solid state and theoretical structures. Z. Kristallogr. **213** (1998) 669–678.
8. Lee, S. M.; Lo, K. M.; Tiekink, E. R. T.: Crystal structure of (2,2′-bipyridyl)bis(4-bromobenzyl)dibromidotin(IV), $C_{24}H_{20}Br_4N_2Sn$. Z. Kristallogr. NCS **234** (2019) 1317–1319.
9. Lee, S. M.; Lo, K. M.; Tiekink, E. R. T.: Crystal structure of (2,2′-bipyridyl)bis(4-chlorobenzyl)dichloridotin(IV), $C_{24}H_{20}Cl_4N_2Sn$. Z. Kristallogr. NCS **234** (2019) 1321–1323.
10. Lo, K. M.; Lee, S. M.; Tiekink, E. R. T.: Crystal structure of dichloridobis(4-chlorophenyl-κC^1)-(1,10-phenanthroline-κ^2N,N')tin(IV), $C_{24}H_{16}Cl_4N_2Sn$. Z. Kristallogr. NCS **235** (2020) 695–697.
11. Turner, M. J.; Mckinnon, J. J.; Wolff, S. K.; Grimwood, D. J.; Spackman, P. R.; Jayatilaka, D.; Spackman, M. A.: Crystal Explorer v17. The University of Western Australia, Australia (2017).
12. Tan, S. L.; Jotani, M. M.; Tiekink, E. R. T.: Utilizing Hirshfeld surface calculations, non-covalent interaction (NCI) plots and the calculation of interaction energies in the analysis of molecular packing. Acta Crystallogr. **E75** (2019) 308–318.